Electrically controllable energy gaps in graphene quantum dots

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We theoretically demonstrate that the energy gaps of graphene quantum dots (GQDs) can be easily tuned by applying opposite electrostatic potentials to the two equally divided parts of them. This control of energy gaps by such an external electrostatic potential can be realized in various sizes or shapes of GQDs. We propose that the physical origin of the gap tunability is the delicate coupling between the two parts of GQDs with opposite electrostatic gate potentials. Our findings are quite useful for the application of GQDs to the electronic devices and photovoltaic devices. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4704918]

Graphene has attracted enormous interest both in theory and experiments, due to its exceptional electronic properties and great application potential in next-generation electronics. The valence and conduction bands of graphene intersect at two inequivalent Dirac points and exhibit linear spectra near these points, so the electrons in graphene behave just like massless Dirac fermions. However, a gap has to be induced in the gapless graphene for its real applications in electronic devices. For this purpose, graphene quantum dots (GQDs) have been proposed as one of the most promising kinds of graphene nanostructures. Due to the Klein tunneling effect of massless Dirac fermions, typical quantum dots cannot be formed in graphene by electrostatic confinement just as in semiconductor heterostructures. On the other hand, the lateral confinement can be formed easily in finite-size graphene flakes.

With recent developments of fabrication techniques, it is possible to accurately cut the bulk graphene into different sizes and shapes, such as hexagonal zigzag GQDs, hexagonal armchair GQDs, triangular zigzag GQDs, and triangular armchair GQDs. The electronic properties of GQDs depend strongly on their sizes and shapes. There appear energy gaps in almost all the energy spectra of GQDs, which decrease monotonously as the number of atoms increases. Moreover, degenerate zero-energy states appear in the energy spectra of triangular zigzag GQDs, which provides opportunities for the simultaneous control of magnetic and optical properties of such nanostructures. The size-dependent energy gaps of GQDs also make them particularly interesting for light harvesting in photovoltaic devices since the absorption edges can be tuned by varying their sizes. However, a more useful and convenient way to tune the energy gaps is by means of an external field. An external magnetic field can tune the energy gaps of GQDs, but very large magnetic field values are needed to see its effects on the energy spectra. So it is an open and interesting problem whether it is possible to tune the energy gaps of GQDs by means of an electrostatic potential.

In this paper, we explore the possibility of controlling the energy gaps of GQDs by the application of electrostatic gate potentials. We equally divide various shapes of GQDs into two parts and then apply opposite electrostatic potentials to the left and right parts, respectively, as in Fig. 1. Surprisingly, we find that the energy gaps of GQDs can be tuned from the original values to almost zero by just tuning the electrostatic potential.

The energy spectra of GQDs can be calculated based on the tight-binding model. The tight-binding Hamiltonian with the nearest-neighbor approximation is

$$\hat{H} = \sum_{n} (e_n + U_n) c_{n}^{\dagger} c_{n} + \sum_{\langle n,m \rangle} (t_{n,m} c_{n}^{\dagger} c_{m} + H.c.),$$

where $e_n$ is the energy of the $n$th site, $U_n$ is the electrostatic potential at the $n$th site, $c_{n}^{\dagger}$ and $c_{n}$ are the creation and annihilation operators at the $n$th site, $t_{n,m}$ is the hopping integral between the $n$th and $m$th sites, and $H.c.$ denotes the Hermitian conjugate.

FIG. 1. Various kinds of GQDs [(a) hexagonal zigzag GQD ($N_z = 3$), (b) hexagonal armchair GQD ($N_a = 4$), (c) triangular zigzag GQD ($N_z = 4$), (d) triangular armchair GQD ($N_z = 6$)] with the application of electrostatic gate potentials. A positive electrostatic gate potential $U$ is applied to the left half parts of the GQDs, while a negative electrostatic gate potential $-U$ is applied to the right half parts of the GQDs. $N_z$ is the number of carbon atoms in each side of GQD.
with

\[ U_n = \begin{cases} U, & \text{in the left half part of GQD}, \\ -U, & \text{in the right half part of GQD}. \end{cases} \]

where \( n, m \) denote the sites of carbon atoms in GQDs, \( E_n \) is the energy of the \( n \)th site, \( U_n \) denotes the external electrostatic gate potential, \( t_{n,m} \) is the hopping energy, and \( c_n^\dagger (c_n) \) is the creation (annihilation) operator of the \( \pi \) electron at site \( n \). The summation is taken over all nearest neighboring sites \( \langle n,m \rangle \). Due to the homogeneous geometrical configuration, the on-site energies and the hopping energies may be taken as \( E_n = E_F = 0, t_{n,m} = t = 2.7 \text{ eV} \). The tight-binding Hamiltonian can also be represented in matrix form and the energy spectrum of GQD can be calculated by diagonalization of the matrix.

Since the fermi energy is chosen to be zero, the energy spectrum must be symmetric between the positive and negative energy states. There is only one electron for each carbon atom, so the band-filling factor is 1/2. For most of the GQDs, there is no zero-energy states, so the system is metallic and the energy gap can be defined as the energy difference between the highest valence level and the lowest conduction level.\(^{11}\) However, for triangular zigzag GQDs, there exist degenerate zero-energy states, so the system is metallic and the energy gap can be defined as the energy difference between the lowest positive state and the zero-energy states.\(^{12}\)

For hexagonal and triangular GQDs, the number of carbon atoms in each side is the same. We define \( N_s \) as the number of carbon atoms in each side of GQD and \( N \) as the total number of carbon atoms in GQD, then we have \( N = 6N_s^2 \) for hexagonal zigzag GQD, \( N = [9N_s(N_s/2 - 1)] + 6 \) for hexagonal armchair GQD, \( N = [(N_s + 2)^2 - 3] \) for triangular zigzag GQD, and \( N = 3N_s(N_s + 2)/4 \) for triangular armchair GQD.

The energy spectrum of hexagonal zigzag GQD with \( N = 384 \) is plotted as a function of the electrostatic potential \( U \) in Fig. 2(a), and the corresponding energy gap \( E_g \) is also plotted as a function of \( U \) in Fig. 2(b). It is shown that \( E_g \) oscillates violently as \( U \) increases and reaches the minimum when \( U \approx t \); when \( U > t, E_g \) oscillates less violently and the mean value keeps almost unchanged. However, the situation is quite different for the hexagonal zigzag GQD with \( N = 366 \) [see Figs. 2(c) and 2(d)]: \( E_g \) decreases almost monotonously from 0.55 eV to 0.05 eV when \( U \) increases from 0 to 1 eV, then it oscillates as \( U \) increases but it is always kept at low value.

As for the triangular zigzag GQD with \( N = 438 \) [see Figs. 3(a) and 3(b)], we find that the degenerate zero-energy states become split when the electrostatic potential \( U \) is applied, and the energy gap \( E_g \) can be tuned almost linearly from 0.77 eV to 0 when \( U \) increases from 0 to 0.55 eV. The situation is quite similar for the triangular armchair GQD with \( N = 396 \) [see Figs. 3(c) and 3(d)], \( E_g \) can also be tuned from 0.71 eV to about 0.04 eV when \( U \) increases from 0 to 2 eV, but there are some small oscillations in the process.

To find the physical origin of the energy gap tunability, we consider the simplest case, i.e., benzene composed of six carbon atoms under the influence of the electrostatic potential similar to Fig. 1. The tight-binding Hamiltonian of benzene with the application of \( U \) in matrix form is

\[
H = \begin{pmatrix}
U & t & t & 0 & 0 & 0 \\
t & U & 0 & t & 0 & 0 \\
0 & t & 0 & -U & 0 & t \\
0 & 0 & t & 0 & -U & t \\
0 & 0 & 0 & t & 0 & -U \\
0 & 0 & 0 & 0 & t & -U
\end{pmatrix}.
\]

The energy spectrum of benzene as a function of \( U \) is plotted in Fig. 4(a), from which we see that the energy gap \( E_g \)
decreases as $U$ increases until it reaches the minimum, then it increases as $U$ increases. Diagonalization of the Hamiltonian of benzene can also give the analytical form of the energy gap as follows:

$$E_g = \sqrt{2U^2 + 10r^2 - 2r\sqrt{32U^2 + 9r^2}}.$$ 

which clearly shows that $E_g$ of benzene can be continuously tuned by the electrostatic potential $U$. For a comparison, we also plot the energy spectrum of triangular armchair GQD as a function of $U$ in Fig. 4(b), where $E_g$ can be tuned to almost zero as $U$ increases.

When we find that the energy gaps of various shapes or sizes of GQDs can be tuned by the electrostatic potential, we may attribute this phenomenon to the two-dimensional honeycomb lattice structure and the resultant Dirac fermions in graphene. However, as the size of GQD decreases, the Dirac fermion behavior of electrons gradually disappears and the quantum dot behavior becomes more and more apparent.

The benzene is just a molecule, but when we apply the electrostatic potential to the benzene, we also find energy gap tunability similar to the GQDs. This shows that the energy gap tunability of GQDs does not originate from the honeycomb lattice structure of graphene, so the energy gap tunability by an external electrostatic potential is universal for various sizes or shapes of GQDs. However, as the size of GQD increases, the relationship between the energy gap and the electrostatic potential becomes complicated due to the increased dimensionality of the Hamiltonian matrix.

The electrostatic potential $U$ can be varied in a much larger range in Fig. 4 than in Figs. 2 or 3. We can see that when $U$ increases above certain large value, the energy spectra of GQD begin to be split into two bands symmetrically around the zero-energy. This means that the left part and right part of GQD are decoupled under the influence of large opposite electrostatic potentials. However, when $U$ is not too large, the left part and right part of benzene or GQD are still coupled together, but the energy spectra are changed due to

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the presence of $U$. So, we conclude that the tunabilities of energy gaps of GQDs originate from the delicate coupling between the two parts of GQDs with opposite electrostatic gate potentials.

In summary, we have demonstrated that the energy gaps of GQDs can be tuned in a large range by applying opposite electrostatic gate potentials to the equally divided two parts of GQDs. We also find that the control of electronic structure by such an external potential is universal for various sizes and shapes of GQDs. We propose that this phenomenon is due to the delicate coupling between the two parts of GQDs with opposite electrostatic gate potentials. Our calculated results demonstrated the possibility to tune the electronic properties of GQDs by the electric field and may be quite useful for the application of GQDs to electronic and photovoltaic devices.

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